

PATENT SPECIFICATION

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DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Process for the Oxychlorination of Organic Compounds.

We, HOOKER CHEMICAL CORPORATION, a Corporation organized and existing under the laws of the State of New York, United States of America, of Niagara Falls, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the oxychlorination of short chain olefins in the presence of an oxychlorination catalyst.

Short chain olefins, such as ethylene, propylene, butylene and the like have been oxychlorinated at temperatures of from about 250 degrees centigrade to about 650 degrees centigrade in the presence of catalysts comprised of chlorides of metals possessing variable valences. Such processes, however, require operating in a temperature range sufficiently high to obtain a fairly high conversion of the olefin. Such high temperatures result in high combustion rates as well as increased side reactions. Thus, if the reaction could be effected at relatively low temperatures, combustion of the olefin could be reduced, and a high yield of product could be achieved, while enhancing the purity of the product by reducing cracking and side reactions.

In accordance with the present invention, there is provided a process for the oxychlorination of alkenes, comprising: a) contacting and reacting at a temperature of from 170 to 400 degrees centigrade in the vapor phase and in the presence of an oxychlorination catalyst: 1. oxygen, 2. an alkene or partially halogenated alkene of 2 to 4 carbon atoms, 3. an inorganic gas as diluent, 4. as chlorinating agent, hydrogen chloride, chlorine, or a mixture of hydrogen chloride and chlorine, the amounts of chlorinating agent being less than that stoichiometrically required to add two chlorine atoms to each molecule of alkene; b) subsequently partially condensing the effluent gases; c) separating the condensate; and d) recycling substantially all of the non-condensed gases, thereby providing additional reactants and diluent gases for further reaction.

The preferred reaction temperature for this process is from 180 to 280 degrees centigrade, while there is used preferably from 50 to 98% of the stoichiometric amount of chlorinating agent.

The diluent gas is most suitably nitrogen, and can also be carbon dioxide; other inorganic diluents may be used.

The present invention provides a continuous process for chlorinating alkenes at yields greater than 95 per cent based on the alkene and the chlorinating agent, to a product with a purity of more than 98 per cent. The oxychlorination is effected in a manner which eliminates the requirement of recovering chlorinating agent from the effluent gases thereby reducing initial investment costs and operating expenses. The recovery system for the chlorinated organic product is simplified in that the need for refrigeration units and absorption towers is eliminated, or greatly reduced, due to the fact that all of the chlorinated organic product does not have to be removed; some can be recycled with the recycle gases. The invention provides a recycle operation which greatly reduces the loss of unreacted alkene since substantially all of the unreacted feed gases including the most valuable, the alkene, are recycled for further reaction.

The process is readily described by reference to the accompanying drawing, which is a flow sheet illustrating the present invention. The process is effected by feeding gaseous reactants and dilution gases to

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a reactor 10 wherein they are reacted, passing the effluent gashes from the reactor through the product separator 12, wherein they are cooled and partially condensed thereby forming an organic phase 32 and an aqueous phase 16, and recycling the non-condensed gas phase 14 for further reaction. The feed to the reactor 10 comprises oxygen 42, alkene 40, nitrogen 38, recycle gas 36 and a chlorinating agent 46. The concentration of the gases is regulated and controlled within the preferred ranges, such regulation being in accordance with periodic or continuous analysis made by passing the gases other than the chlorinating agent through an analyzer 44 prior to entering the reactor 10. In accordance with the analysis, the preferred ratios of reactants and diluents are accurately achieved.

Many methods of analyzing the gas constituents flowing into the reactor can be used including continuous gas chromatography analysis, periodic gas chromatography analysis, as well as periodic sampling of the gases with subsequent analysis by suitable analytical methods. The sampling and analysis can be effected on either the feed gas mixture or the recycle gas. Due to the interference of the chlorinating agent with analytical determinations, it is normally preferable to add the chlorinating agent to the gas feed stream subsequent to analysis sampling.

The proportions of oxygen, alkene, diluent gas and recycle gas are regulated to avoid danger of reaching the explosive limits of the various mixtures. Because the present process involves recycle of gaseous reactants, including carbon monoxide, the explosive limits of such mixtures are affected by the concentrations of oxygen, carbon monoxide and alkene, as well as the presence or absence of non-flammable diluents. Thus, it is seen that both the feed gas mixture and the recycle gas mixture should be controlled to be outside their explosive limits.

It has been found that the feed gas mixture, on a chlorinating agent free basis, is best regulated between the volume per cent limits of 1 to 20 per cent oxygen, 3 to 55 per cent nitrogen, 1 to 20 per cent carbon dioxide, 20 to 80 per cent alkene (based on ethylene) and 1 to 12 per cent carbon monoxide, the preferred range being 3 to 15 per cent oxygen, and 40 to 75 per cent alkene (based on ethylene).

The alkenes oxychlorinated by the present invention, are alkenes of 2 to 4 carbon atoms as well as their partially halogenated derivatives. Illustrative examples of such alkenes include ethylene, propylene, 1-butylene, 2-butylene and vinyl chloride. Of the alkenes named, ethylene is preferred and

the preferred reaction is the oxychlorination of ethylene to 1,2-dichloroethane.

The chlorinating agent utilized can be any which will not adversely affect the reaction mechanism as described herein. Such compounds as hydrogen chloride, chlorine, and mixtures of chlorine and hydrogen chloride can be used. The preferred chlorinating agent is hydrogen chloride. The chlorinating agent is used in less than the stoichiometric amount, based on adding two chlorine atoms to the alkene. As stated, the chlorinating agent is preferably used in an amount of 50 to 98 per cent stoichiometric, based on the total alkene in the reactor.

To provide nitrogen as a diluent gas, there is preferably used pure nitrogen. However, mixtures of nitrogen and oxygen, such as air, can be used, but are less convenient in providing close control of the gas ratios. This is especially true in the present process wherein only minor amounts of nitrogen need be periodically added. Since nitrogen is not consumed in the reaction, the loss from the reaction system is very small. In addition to, or in place of nitrogen, other non-reactant and non-flammable gases, such as CO₂ and argon can be used as diluent.

The recycle gas 36 is comprised primarily of unreacted alkene, carbon dioxide, carbon monoxide, oxygen and nitrogen. The proportion of feed gases are controlled so that the recycle gas does not reach an explosive limit. Normally, the oxygen content of the recycle gases will range between 1 and 20 volume per cent and more preferably 1.5 to 16 per cent by volume. The carbon monoxide level is preferably maintained below about 20 per cent by volume. The remaining constituents of alkene, carbon dioxide and nitrogen comprise the remaining volumes of the recycle gas. These gases are present in the ranges by volume of 1 to 15 per cent carbon monoxide, 2 to 25 per cent carbon dioxide, 3 to 70 per cent nitrogen and 4 to 80 per cent alkene (based on ethylene) determined on a basis free of chlorinating agent.

The reactor 10 is preferably a fluidized bed. In the utilization of a fluidized bed, the gaseous reactants are fed, in varying velocities, to the reactor so as to effect a fluidization of the catalyst particles in the reactor. The fluidization is effected in a conventional manner by causing the gas feed stream to proceed from the bottom of the catalyst bed or reactor, to the top. Cylindrical reactors of greater height than diameter are normally employed.

Effective fluidization is achieved by using a finely divided solid catalyst having particle sizes in the range of 0.30 to 0.003 inch diameter. By controlling the velocity of the gaseous reactants with respect to the par-

5 ticle sizes used, the catalyst particles are placed dynamically in suspension in the rising flow of gases, thereby circulating and otherwise behaving like a fluid, such as a liquid. Various other factors to be considered in establishing fluidized beds are described in an article by Wilhelm and Kwauk in "Chemical Engineering Progress", Volume 44, page 201.

10 The process can alternatively be effective, in a fixed bed where tubular or elongated reactors are used having a high length to inner diameter ratio. For example, the inner diameter of such a reactor is usually small compared to the length of the reactor which may be 1 to 500 times as large as the inner diameter. When such stationary bed reactors are used, it is preferred to dilute the catalyst with inert material to control the temperature of reaction and dissipate the heat generated.

15 The reaction carried out in the fluidized bed is an oxychlorination reaction. The term "oxychlorination" means a catalyzed chlorination process wherein a catalyst and a chlorinating agent are contacted with an organic reactant in the presence of oxygen, thereby effecting the chlorination of the organic reactant. It is believed that in one aspect of this oxychlorination process, the chlorinating agent is produced by oxidation of, for example, hydrogen chloride, which is oxidized to chlorine and water, followed by the reaction of the chlorine with organic reactant to form a chlorinated organic compound.

20 The catalyst used in the process of the present invention may be an oxychlorination catalyst, such as a metal halide, particularly copper chloride or iron chloride. The oxychlorination catalyst is prepared in a form, such as a solid granule as previously described, suitable for fluidization. While many different oxychlorination catalysts can be used in the present process, the preferred catalyst is a co-precipitated complex of alumina and a salt of one or more metals, notably copper, having a variable valence. It has been found that the copper-alumina complex hereafter described has the desired physical and chemical characteristics of outstanding durability and catalytic activity particularly useful in a fluidized bed at the preferred temperatures. In our Specification No. 1,106,234 we describe a process for the oxychlorination of alkanes and alkenes, without recycle, in which the same catalyst is used.

25 In place of copper in the preferred catalyst, or in addition thereto, one or more metals of Group III to VIII of the Periodic Table which possess variable valences, such as scandium, titanium, vanadium, nickel, chromium, cobalt, iron and uranium, can be used as an ingredient of

the catalyst. Silver and gold are further alternative ingredients. The preferred catalyst, however, is comprised of a major proportion of alumina (Al_2O_3) and a minor, but effective proportion of combined copper, the remainder of the catalyst, if any, being substantially inert materials which may be merely impurities. Generally, this complex copper-alumina catalyst contains from 65 per cent to 99 per cent alumina and from 1 per cent to 35 per cent copper or other metal as described. The preferred range is from 80 per cent to 90 per cent alumina and 5 per cent to 15 per cent copper. Of course, lesser and greater amounts of copper and alumina may also be effective in certain operations.

30 The preferred catalyst is a porous solid of high mechanical, chemical and thermal stability under the reaction conditions. The catalyst is used in the form of particles, granules, chips or pellets with the granular form being preferred, particularly in the fluidizing size previously described. Inert solid diluents, such as carbon, e.g. graphite, can also be mixed therewith if desired.

35 The copper-alumina complex is prepared by causing alumina hydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and cupric chloride to coprecipitate, as by the addition of acid, in sufficient proportions to result in a catalyst composition containing the desired proportions of copper and alumina. The precipitated complex is filtered from the mother liquor, washed, dried, and subsequently roasted at a temperature of 200 degrees centigrade to 400 degrees centigrade. The resulting product is a hard porous material, normally greenish in color, having a specific gravity greater than one. The product is then broken or ground into the desired particle size.

40 Other metal complexes, similar to the copper-alumina complex, which are useful as catalysts, in the present invention, are prepared in the same manner by precipitating alumina hydrate in an aqueous solution with a chloride of a variable valence metal, by the addition of an acid such as hydrochloric acid. Thus, the copper-alumina complex may be formed with copper and an additional metal of variable valence to form the metal-alumina complex.

45 The temperature employed for effecting the process of the present invention in the reactor is in the range of about 170 to 400 degrees centigrade and preferably in the range of 180 degrees centigrade to 280 degrees centigrade.

50 The effluent gases from the reactor are passed through the product separator which provides a condensing zone wherein the water of reaction, residual chlorinating agent, and chlorinated organics are condensed and separated as liquids. The condenser is controlled at a temperature sufficient

cient to effect the condensation of an aqueous phase and an organic phase of chlorinated organics, while the unreacted gases pass through the product separator 12. The unreacted gases comprise primarily alkene, which is fed to the reactor in an excess, nitrogen, oxygen, carbon dioxide and carbon monoxide. These gases are considered to be non-condensable gases in the present process in that they have dew points substantially less than that of water and that of the chlorinated organics produced by the present process. Normally, the condensation of the aqueous and organic phase is effected using cooling water, super cooled water, brine and other conventional heat exchange media.

In the product separator 12, three phases are separated; a gas phase 14 which passes through product separator 12 to be subsequently recycled to the reactor, an aqueous phase 16 which comprises water and unreacted hydrochloric acid and an organic phase 32 which contains the chlorinated organic. The aqueous phase 16, under the conditions of the present process contains primarily water with minor percentages of hydrochloric acid. A particularly valuable feature of the present invention is in operating in a manner such that the aqueous phase contains only minor amounts of hydrochloric acid and, therefore, can be conveniently disposed of without requiring an additional step of recovering the hydrochloric acid from the aqueous phase.

The organic phase 32 comprises the chlorinated organic in a very high state of purity, normally greater than 99 per cent. This product can be subsequently further purified, if desired.

The gas phase 14, is recycled via line 15 to compressor 22. Along line 15 is waste gas vent 18 which vents a small proportion of gas phase 14. Waste gas vent 18 has pressure controlling means for regulating the pressure within the reaction system. Thus, the pressure is controlled near atmospheric or somewhat higher. The pressure can also be controlled somewhat below atmospheric. Normally, waste gas vent 18 permits 0.1 to 5 per cent of the gas phase to be vented thereby also controlling the degree of accumulation of nitrogen, carbon dioxide and carbon monoxide. Thus, substantially all of the effluent gases are recycled to the reactor.

Compressor 22 and condenser 24 provide means of further condensing and removing the aqueous and organic phases. The additional condensate is removed from the gas stream in separator 26 and routed to the organic phase 32 and aqueous phase 16. In addition to effecting a further separation of the aqueous and organic phases, the compressor 22 provides pressure for the recycle

gas 36, thereby providing means for returning the non-condensable gases to the reactor 10.

From separator 26, gas phase 28 is passed via line 31 to gas flow control 34 which controls the flow rate of recycle gas 36.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practised, the following illustrations and examples are given. Unless otherwise indicated, all temperatures are in degrees centigrade and all parts and percentages used herein are by weight.

EXAMPLE 1:

1,2-Dichloroethane was produced by the method of this invention as described in the drawing. The process was commenced by feeding essentially pure hydrogen chloride, oxygen and ethylene to a tubular, fluidized-bed reactor containing 477 parts of a coprecipitated copper-alumina complex. The copper-alumina complex comprised about 7 per cent copper, the remaining percentage being substantially alumina. The catalyst was used in a particle size of 80 to 140 U.S. Sieve. The reactant gases were fed to the reactor at a rate sufficient to obtain a fluidized bed height of about 7 1/2 times the internal diameter of the reactor. In the reactor used, the feed rate corresponded to a gas flow of 730 standard volumes per minute of HCl, 193 standard volumes per minute of oxygen, 354 standard volumes per minute of ethylene and 1,950 standard volumes per minute of recycle gas. This feed rate corresponded to an average molar ratio of 1.955 moles of HCl, 0.516 moles of oxygen, 0.949 moles of ethylene and 5.22 moles of recycle gas.

The exothermic reaction was controlled in the temperature range of 190 degrees centigrade, plus or minus 5 degrees centigrade.

The effluent gases from the reactor were passed through the product separator wherein the condensation of 68.8 parts per hour of organic product and 19.3 parts per hour of aqueous condensate was effected. Gases passing through the product separator were subsequently compressed and condensed to yield additional organic product at the rate of 25.8 parts per hour and aqueous condensate at the rate of 1.02 parts per hour. In total, organics were recovered at the rate of 94.6 parts per hour and an aqueous phase was recovered at the rate of 20.3 parts per hour. The gases passing through the compressor and condenser were recycled to the reactor. These gases were analyzed and found to have an average composition by volume of 5.5 per cent oxygen, 40.2 per cent nitrogen, 16.0 per cent carbon dioxide, 29.2 per cent ethylene and 9.1 per cent

carbon monoxide. Since nitrogen is not consumed in the reaction, but rather continuously recycles, its content is controlled by periodic additions, thereby retaining the nitrogen content at the average amount indicated.

During the reaction, the pressure in the reaction system was controlled at about atmospheric pressure by venting recycle gases at an average rate of 18.2 standard volumes per minute, which corresponds to less than 1.0 per cent of the recycle gases.

Gas chromatography analysis of the organic phase recovered gave the following results:

Ethylene dichloride ...	99.5	per cent
Perchloroethylene ...	0.45	per cent
Trichloroethylene ...	trace	
Dichloroethylene ...	trace	
Ethyl chloride ...	trace	
H ₂ O ...	trace	
HCl ...	trace	
Trichloroethane ...	trace	

The recovered aqueous layer was also analyzed and found to contain 11.5 per cent by weight of HCl.

The process yield of ethylene dichloride was 97.5 per cent per mole of ethylene, 92.1 per cent per mole of oxygen fed to the reactor and 96.4 per cent per mole of HCl fed to the reactor. It is to be noted that in addition to the extremely high purity of the product obtained by the present process, the process is highly efficient as is noted by the process yields.

EXAMPLE 2:

Ethylene dichloride was produced by the continuous process of the present invention in accordance with the drawing as follows: The reaction was commenced by feeding hydrogen chloride, oxygen, ethylene and recycle gases to a fluidized bed reactor. The fluidized bed height was about 3 1/2 times the inside diameter of the reactor. The catalyst comprised 224 parts of a co-precipitated copper-alumina complex containing 8.71 weight per cent copper and 45.91 weight per cent aluminum as aluminum oxide. The catalyst was of a particle size of 80 to 140 U.S. Standard Sieve (through No. 80 mesh and retained on 140 mesh). The data obtained in the reaction was the average of continuous operation for 96 hours.

The gases fed to the reactor comprised 729 standard volumes per minute of HCl, 193 standard volumes per minute of oxygen, 358 standard volumes per minute of ethylene and 1950 standard volumes per minute of recycle gas.

This feed rate corresponded to a mole ratio of 1.955 moles of hydrogen chloride,

0.516 moles of oxygen, 0.958 moles of ethylene, and 5.22 moles of recycle gas.

The reaction of the gases on contact with the fluidized catalyst was effected at a temperature of 210 degrees centigrade plus or minus 5 degrees centigrade. The effluent gases from the reactor were passed through the product separator wherein the produced organics and an aqueous phase were condensed and separated.

Organic product was collected by the product separator at a rate of 67.2 parts per hour while an aqueous phase was collected at a rate of 19.1 parts per hour. The effluent gases from the product separator were passed to a compressor and condenser wherein an additional 26.3 parts per hour of organic product and 1.06 parts per hour of aqueous product were collected and separated. In total, organic product was recovered at a rate of 93.5 parts per hour while an aqueous phase was recovered at a rate of 20.2 parts per hour.

The gases emerging from the compressor and condenser were returned to the reactor as recycle gases. Analysis of the gases recycled to the reactor, were found to comprise, by volume, 11.7 per cent oxygen, 20.8 per cent nitrogen, 33.9 per cent carbon dioxide, 19.6 per cent ethylene and 14.0 per cent carbon monoxide. The amount of nitrogen periodically added, resulted in the nitrogen level indicated. The carbon dioxide and carbon monoxide levels in the recycle gas were controlled by venting 10.6 standard volumes per minute of recycle gas from the system. This corresponds to about 0.5 per cent of the recycle gases.

Gas chromatography analysis of the recovered organic phase gave the following results:

Ethylene dichloride ...	99.5	per cent
Perchloroethylene ...	0.3	per cent
Trichloroethylene ...	0.1	per cent
Dichloroethylene ...	trace	
Ethyl chloride ...	trace	
Water ...	trace	
HCl ...	trace	
Trichloroethane ...	0.1	per cent

Analysis of the aqueous phase indicated that the HCl content was 10.36 weight per cent, the remaining being substantially water.

The process yields, based on ethylene dichloride were 97.9 per cent per mole of ethylene fed to the reactor, 90.8 per cent based on the oxygen fed to the reactor, and 96.5 per cent based on the hydrogen chloride fed to the reactor.

EXAMPLE 3:

This example illustrates the production of 1,2-dichloroethane by the continuous recycle

reaction of the present invention. The present example was again run, as were the other examples, with a molar deficiency of hydrogen chloride based on the total ethylene in the reactor thereby effecting a high percentage reaction with hydrogen chloride in a single pass through the reactor.

The reaction was effected in a reactor similar to that of Example 1 using the same type and amount of catalyst. The reaction temperature was controlled at 200 degrees centigrade. The catalyst was fluidized by a reactor feed stream of 198 standard volumes per minute of oxygen, 750 standard volumes per minute of hydrogen chloride, 354 standard volumes per minute of ethylene and 1950 standard volumes per minute of recycle gas. Analysis of the feed gas on a HCl free basis indicated that it comprised, by volume, 14.8 per cent oxygen, 42.6 per cent nitrogen, 11.3 per cent carbon dioxide, 25.3 per cent ethylene and 6.0 per cent carbon monoxide.

The reaction was run continuously for 150 hours during which time the effluent gases from the reactor were condensed and separated in an amount of 92.0 parts per hour of organic product and 20.4 parts per hour of aqueous product.

The effluent gases from the condensing zones were recycled to the reactor. These recycle gases comprised by volume, 16.0 per cent oxygen, 57.6 per cent nitrogen, 13.4 per cent carbon dioxide, 6.6 per cent ethylene and 6.4 per cent carbon monoxide.

Analysis of the organic phase showed that it contained 99.4 per cent ethylene dichloride. The separated aqueous phase contained 13.1 per cent hydrogen chloride, the remaining being substantially water. The yield of ethylene dichloride was 98 per cent based on the amount of ethylene fed to the reactor, 92.5 per cent based on the amount of HCl fed to the reactor and 87.6 per cent based on the amount of oxygen fed to the reactor. The hydrogen chloride efficiency, based on the hydrogen chloride recovered, was 96.1 per cent.

EXAMPLE 4:

Ethylene dichloride was again produced by the method of the present invention using a reactor and catalyst similar to that of Example 2. The reaction was conducted at a temperature of 190 degrees centigrade in a fluidized bed. The gaseous reactants were fed to the reactor in a steady stream of sufficient pressure to effect the fluidization of the catalyst in the reactor. The reactor feed stream comprised 193 standard volumes of oxygen per minute, 780 standard volumes per minute of hydrogen chloride, 354 standard volumes per minute of ethylene and 1950 standard volumes per minute of recycle gas. This composition, on a

chlorine free basis, resulted in a mixture by volume of 8.1 per cent oxygen, 7.7 per cent nitrogen, 13.6 per cent carbon dioxide, 63.5 per cent ethylene and 7.2 per cent carbon monoxide.

The effluent gases from the reactor were passed through a condenser and subsequently through a second high pressure condenser, thereby effecting the separation of an aqueous phase, consisting of 18.1 parts per hour, and an organic phase consisting of 90.4 parts per hour. The effluent gases from the condensers were recycled to the reactor for further reaction. Analysis of the recycled gases indicated that they comprised by volume, 2.4 per cent oxygen, 8.3 per cent nitrogen, 19.3 per cent carbon dioxide, 61.1 per cent ethylene and 8.9 per cent carbon monoxide.

Gas chromatography analysis of the recovered organic phase indicated that it contained 99.6 per cent ethylene dichloride. Analysis of the aqueous phase indicated that it contained 2.4 per cent hydrogen chloride, the remainder being substantially water.

The yield, based on ethylene dichloride, was 96.3 per cent based on the amount of ethylene fed to the reactor, 87.4 per cent based on the amount of HCl fed to the reactor and 88.2 per cent based on the amount of oxygen fed to the reactor.

The examples have illustrated the highly efficient process of the present invention and the wide latitude of variance in the gaseous reactants used, wherein the chlorinating agent is used at less than an equal molar ratio with the alkene. It is also apparent that alkenes other than ethylene would be equally as effective as feed material, to effect an oxychlorination of such alkenes in substantially the same manner as that of the examples. Thus, propylene, 1-butylene, 2-butylene and vinyl chloride are readily chlorinated to the respective polychloroalkanes. Also, the reaction is readily effected in the presence of acetylene in the feed material thus resulting in the chlorination of acetylene. (The oxychlorination of acetylene itself is the subject of our co-pending Application No. 38223/66 (Serial No. 1,141,370)). The reaction can also be run under pressures up to about 50 pounds per square inch gauge or more. It will be further recognised by those skilled in the art that other than the preferred oxychlorination catalysts would be effective in the present process. However, the preferred catalyst described herein, has been found to be most effective as a long term high conversion catalyst.

WHAT WE CLAIM IS:—

1. A process for the oxychlorination of alkenes, comprising:

- a) contacting and reacting at a temperature of from 170 to 400 degrees centigrade in the vapor phase and in the presence of an oxychlorination catalyst:
1. oxygen;
 2. an alkene or partially halogenated alkene of 2 to 4 carbon atoms;
 3. an inorganic gas diluent;
 4. as chlorinating agent, hydrogen chloride, chlorine, or a mixture of hydrogen chloride and chlorine, the amounts of chlorinating agent being less than that stoichiometrically required to add two chlorine atoms to each molecule of alkene.
- b) subsequently partially condensing the effluent gases;
- c) separating the condensate; and
- d) recycling substantially all of the non-condensed gases, thereby providing additional reactants and diluent gases for further reaction.
2. A process as claimed in Claim 1, wherein the reaction temperature is from 180 to 280 degrees centigrade.
3. A process as claimed in Claim 2, wherein from 50 to 98 per cent of the stoichiometric amount of chlorinating agent is used.
4. A process as claimed in any preceding Claim, in which the oxychlorination catalyst is a co-precipitated complex of alumina and a salt of one or more metals having a variable valence.
5. A process as claimed in Claim 4, wherein the metal in the catalyst is copper.
6. A process according to Claim 5, wherein the catalyst is a complex co-precipitated copper-alumina catalyst comprising as a major active ingredient alumina and as a minor active ingredient combined copper.
7. A process as claimed in any preceding Claim, wherein said alkene is ethylene.
8. A process as claimed in any preceding Claim, wherein the diluent is nitrogen, argon or carbon dioxide.
9. A process according to any preceding Claim, wherein the recycle gases contain by volume, 1 to 15 per cent carbon monoxide, 2 to 25 per cent carbon dioxide, 1 to 20 percent oxygen, 3 to 70 per cent nitrogen and 4 to 80 per cent alkene, calculated as ethylene).
10. A process according to any one of the preceding Claims, wherein the gaseous mixture contacted with the oxychlorination catalyst comprises, by volume, on a hydrogen chloride-free basis, 1 to 20 per cent oxygen, 3 to 55 per cent nitrogen, 1 to 20 per cent carbon dioxide, 20 to 80 per cent ethylene and 1 to 12 per cent carbon monoxide, hydrogen chloride as chlorinating agent being present in an amount of 50 to 98 per cent of the stoichiometric amount based on ethylene.
11. A process according to Claim 10, wherein the gaseous mixture includes, on a hydrogen chloride-free basis, 3 to 15 per cent by volume oxygen and 40 to 75 per cent by volume ethylene.
12. A process for the oxychlorination of alkenes according to Claim 1, substantially as hereinbefore described.
13. Chlorinated organic compounds when prepared by the process claimed in any one of the preceding Claims.

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